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SYNTHESIS OF ELEMENTO-ORGANIC COMPOUNDS OF ALIPHATIC SERIES
BY DIAZO METHOD IN USSR. SYNTHESIS OF COMPOUNDS OF GROUP V ELEMENTS

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Presented by Acad A. N. Nesmeyanov, 17 Jan 1950

Although the synthesis of elemento-organic compounds over aromatic diazo compounds has been widely investigated for a number of metals and metalloids, an analogous method of synthesis in the aliphatic series by using aliphatic diazo compounds has been known only in the case of mercury.

Hellerman and Newman (1) showed that, as a result of the reaction of diazomethane and phenyldiazomethane with mercury halides, alpha-haloidalkylmercury compounds are formed; similarly, Nesmeyanov and G. Povkh (2) reacted ethyldiazoacetate with mercuric chloride.

Subsequently, a number of authors tried to prepare organic derivatives of zinc (3), iron (4), tin (4), and phosphorus (5) by using aliphatic diazo compounds but all these attempts ended unsuccessfully, tending to give the impression that the synthesis of mercury organic compounds over aliphatic diazo compounds is an exception. The possibility of this conclusion was eliminated by Yakubovich and another collaborator (6) when they prepared aliphatic organic compounds of arsenic.

The purpose of this article is the further clarification of the possibilities and conditions of synthesis of the various elemento-organic compounds of the aliphatic series by the diazo method; and to this end organic compounds of three elements of group V were investigated.

Chlorides of trivalent arsenic, antimony, and bismuth, at a temperature of from 0 to plus 5 degrees centigrade readily interact with aliphatic diazo compounds to form corresponding alpha-haloidoalkyl derivatives, according to the following reaction scheme (where E is As, Sb, or Bi):

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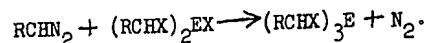
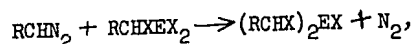
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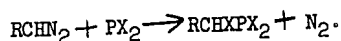
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By using various aliphatic diazo compounds, alpha-haloalkyl derivatives with different aliphatic radicals can be prepared. Generally a mixture of mono-, di-, and tri-alkyl derivatives of the elements is formed, depending on the ratio of the original reacting substances. An increase in the quantity of the diazo compound leads to a predominance of secondary and tertiary products; an excess of the chloride, to a predominance of primary compounds. The yields are 30-50 percent of the theoretical (with respect to the diazo compound).

Similarly, diazo aliphatic compounds interact with phosphorus trichloride or tribromide. In this case, when the reaction is conducted at low temperatures (minus 50 degrees to minus 60 degrees), alpha-haloalkylphosphindihalides are formed with a yield of 40 percent, according to the following reaction scheme:



As a result of the interaction of alkylphosphindihalides with aliphatic diazo compounds, as in the reaction between PX_3 and RCHN_2 at very high temperatures, solid phosphorus organic compounds of a structure more complicated than expected are formed.

Oxyhalides of pentavalent phosphorus of the type POX_3 , (POCl_3 and POBr_3) do not interreact with aliphatic diazo compounds. However, with phosphorus pentachloride the di- and tri- (alpha-haloalkyl) derivatives of pentavalent phosphorus are readily formed.

The reaction of diazo aliphatic compounds with halides of elements of Group V is generally applicable and must serve as a convenient means of synthesizing the little known and difficultly accessible alpha-haloalkyl derivatives of these elements.

The aliphatic diazo compounds necessary for these syntheses were prepared in an ether or benzene solution and were dried by freezing out over caustic soda at minus 70 degrees and then by letting them stand over sodium wire. To prepare the previously described alpha-haloalkyl elemento-organic derivatives, the aliphatic diazo compound was added under stirring to the halide dissolved in ether or benzene. When the reaction was completed (that is, when nitrogen was no longer evolved and the solution became colorless) the solvent was removed and the products of the reaction were distilled.

The table below gives the compounds prepared in this particular investigation (submitted 23 December 1949) and describes their properties:

Formula of Substance	Melting Pt (in °C)	Boiling Pt in °C/P in mm	d_{20}^{20}	n_D^{20}
$(\text{CH}_3\text{CHCl})_2\text{AsCl}$	--	51.5°/1	1.553	1.5870
$(\text{CH}_3\text{CHCl})_3\text{As}$	--	81.82°/2	$d_4^{20} = 1.445$	$n_D^{25} = 1.5307$
ClCH_2BiO	Readily decomposes, sometimes with an explosion. Hydrolyses under conditions of reaction, forming oxide			
$\text{ClCH}_2\text{SbCl}_2$	36-38	86.5°/2	2.677	--

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Formula of Substance	Melting Pt (in °C)	Boiling Pt in °C/P in mm	d_{20}^{20}	n_D^{20}
$(ClCH_2)_3Sb$	--	105°/3	2.038	--
$(ClCH_2)_3SbBr_2$	90-90.5	--	--	--
$(CH_3CHCl)_2SbCl$	--	69.5°/1	1.831	--
$(CH_3CHCl)_2SbOOH$	Did not melt at 190	--	--	--
$ClCH_2PCl_2$	--	80°/140	1.5289	1.5247
$CH_3CHClPCl_2$	--	64°/50	1.4232	1.5090
$ClCH_2PCl_4^*$	102-104 Decomposes	--	--	--
$CH_3CHClPCl_4$	Decomposes	--	--	--
$ClCH_2POCl_2$	--	103°/30	1.6444	1.4945
$CH_3CHClPOCl_2$	--	70°/8	1.5424	1.4930
$CH_3(CH_2)_2CHClPOCl_2$	--	84°/25	1.3236	1.5010
$ClCH_2PO(OH)_2$	92	--	--	--
$ClCH_2PO(OH)_2 \cdot C_6H_5NH_2$	183 Decomposes	--	--	--
$CH_3CHClPO(OH)_2$	100	--	--	--
$ClCH_2PO(OC_2H_5)_2$	--	86°/3	1.1909	1.4360
$CH_3CHClPO(OC_2H_5)_2$	--	93°/5	1.1474	1.4370
$CH_3CHClPO(NHC_6H_5)_2$	154-155	--	--	--
$BrCH_2PBr_2$	--	70°/4	2.6357	--
$BrCH_2POBr_2$	38	112°/2	2.7030	1.6120
$BrCH_2PO(OH)_2 \cdot C_6H_5NH_2$	187 Decomposes	--	--	--
$BrCH_2PO(OC_2H_5)_2$	--	99°/1	1.4474	1.4587
$(ClCH_2)_3PO^{**}$	100.5			
$(CCl_3)_3P^{OH}$	203 Decomposes	--	--	--
$(CH_3CHCl)_2POOH$	107	--	--	--
$(CH_3CHCl)_2POOH \cdot C_6H_5NH_2$	160 Decomposes	--	--	--
$(CCl_3)_3PO$	53	--	--	--

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*This compound is readily chlorinated to CCl_3PCl_4 , which as a result of hydrolysis forms the stable acid semichloride $\text{CCl}_3\text{PO}(\text{OH})$ with m.p. 79 degrees. Trichloromethyl-phosphonic acid can be prepared by hydrolyzing with HCl (in a sealed tube) either this acid semichloride or the diethyl (on methyl) ester of trichloromethylphosphonic acid described by Kamay (7). The melting point of $\text{CCl}_3\text{PO}(\text{OH})_2 \cdot \text{H}_2\text{O}$ is 87 degrees.

**This compound was described earlier (8) as its hydrate, melting point 88-89 degrees.

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